BIODIESEL PRODUCTION VIA HOMOGENEOUS LEWIS ACID CATALYZED TRANSESTERIFICATION

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ABSTRACT

The transesterification of triglyceride mostly found in vegetable oils with methanol using homogeneous lewis acid is one of promising method to convert triglyceride into fatty acid methyl ester which is an alternative to replace fossil fuel as energy source mostly in transportation industry. This study aimed to determine the conversion of fatty acid methyl ester and also to determine the optimum conditions for the production of methyl ester via transesterification process using aluminium chloride as the catalyst and methanol as solvent. By using conventional catalyst such as NaOH and KOH, it formed soap via saponification process and produce huge amount of wastewater in order to separate the reactant and product. Scopes for this research including the effect of molar ratio methanol to oil, effect of reaction temperature and effect of catalyst concentration. After experiments have been done, the most optimum conditions for sunflower oil transesterification can be achived at reaction temperature is 100°C, molar ratio 12:1 methanol to oil and 5 g of aluminium chloride. The highest conversion from these conditions is 91% conversion of fatty acid methyl ester.

ABSTRAK

Pengtransesteran trigliserida banyak ditemui di minyak sayuran dengan metanol menggunakan asid homogen Lewis yang merupakan salah satu cara untuk menukar trigliserida menjadi metil ester asid lemak yang merupakan alternatif untuk menggantikan bahan bakar fosil sebagai sumber tenaga terutama dalam industri pengangkutan. Penelitian ini bertujuan untuk menentukan penukaran metil ester asid lemak dan juga untuk menentukan keadaan optimum untuk pengeluaran metil ester melalui proses pengtransesteran menggunakan aluminium klorida sebagai mangkin dan metanol sebagai pelarut. Dengan menggunakan mangkin konvensional seperti NaOH dan KOH, ianya menyebabkan pembentukan sabun melalui proses saponifikasi dan menghasilkan sejumlah besar sisa air dalam usaha untuk memisahkan reaktan dan produk. Skop penelitian ini termasuk pengaruh nisbah molar metanol minyak, pengaruh suhu dan pengaruh reaksi konsentrasi mangkin. Setelah percubaan telah dilakukan, keadaan yang paling optimum untuk pengtransesteran minyak bunga matahari dapat dicapai pada suhu reaksi 100 ° C, nisbah molar metanol 12:1 untuk minyak dan 5 g aluminium klorida. Penukaran tertinggi dari keadaan ini adalah penukaran 91% metil ester asid lemak.

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LIST OF SYMBOLS

T	-	Temperature
°C	-	Degree Celcius
ml	-	Mililiter
kJ	-	KiloJoule
min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
rpm		Revolutions per minute
M		Molar (mol/dm^3)
FFA	-	Free Fatty Acid

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CHAPTER 1

INTRODUCTION

The whole world is slowly accepting the fact that the main source for fuel and energy are rapidly depleted. The major energy supplier for the whole world is petroleum derived fuel that has wide range of industry application. Oil geologists, oil company executives and most scientists know the fact that an oil crisis is nearly upon us. World peak oil production is about to happen whether in a few years or within the decade, world oil production will decline. Peak oil is the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. Eventually, some of the world's oil producing regions has already experienced steep declines. It happened in the US in 1971. It happened in the North Sea in 1999. It happened in Mexico in 2006.

Generally, biodiesel is a non-toxic, biodegradable and greenhouse gas neutral. Modern diesel engine technology has advanced to the point where the advantages of biofuel usage are becoming much greater than the disadvantages such as less noise, smoke or vibrations and they are more fuel-efficient than older model engines. Besides, diesel engines have the added advantage of greater acceleration when compared to gasoline engines on the same model of vehicle.

Basically, diesel fuel is one of the petroleum based fuels. It has variety of application especially in transportation and development of country. Moreover, diesel is widely used for agriculture purpose and equipment like tractors and trucks and also other application that involve the uses of machinery equipment. Unluckily, the price of diesel fuel is not really constant and until today, the price of diesel issue for every consumer because the increasing of diesel fuel gives a huge impact. Eventually, researches came up with some fresh new ideas to develop an alternative to replace the current energy source. A lot of effort has been carried out such as methanol, ethanol, hydro power, solar energy and geothermal energy as energy sources while for transportation vehicle system, liquefied petroleum gas (LPG), liquefied natural gas (LNG), reformulated gasoline, reformulated diesel fuel have been considered as an alternative way for replacing diesel fuel.

Human caused global warming is one of the greatest and the most urgent challenges facing humanity and life on earth today. The main culprit is the enormous amount of the potent greenhouse gas carbon dioxide (CO_2) released into the atmosphere by burning of fossil fuels (petroleum, coal, natural gas). Burning fossil fuels releases more than 6 billion tons of CO_2 per year, twice as much as the biosphere can absorb. The excess of CO_2 is clogging the atmosphere, with the result that less solar heat is reflected away, more heat reaches the earth's surface, and global temperatures rise. In term of environment benefit, biodiesel contains no sulfur or aromatics, and use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. U.S. Department of Energy study showed that the production and use of biodiesel, compared to petroleum diesel, resulted in a 78.5% reduction in carbon dioxide emissions.

1.1 Background of study

The most feasible alternative that can replace our source of fuel lately is by using the extracted oil from plant origin such as from vegetable oil or animal fats and react it with amount of alcohol through transesterification process. This feasible method produces biodiesel. Basically, biodiesel defined as fuel made from natural, renewable sources, such as new and used vegetable oils and animal fats, for use in a diesel engine or the process that involves reacting vegetable oils or animal fats catalytically with a short-chain aliphatic alcohols.

There are main several advantages for using the biodiesel which are renewable, cheaper than petrodiesel, not acquire an engine modification, not harmful to environment, can make vehicle perform better, reduce the environment effect of waste product, high energy efficiency, and the most important is biodiesel can be produced locally. Biodiesel is surely a viable fuel alternative. Moreover, it is also a sustainable fuel. Using biodiesel not only helps maintain our environment, it also helps in keeping the people around us healthy. The production of biodiesel all over the world is now being looked upon favorably. In Europe, many biodiesel stations have been set up already. There is also a move to convert or make cars compatible with biodiesel fuel in the near future.

Today, there are multiple operating options available for making biodiesel. Many of these technologies can be combined under various conditions and feedstock in an infinite number of ways. The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery. One of the technologies is by using ultrasound technologies**.** The ultrasonic mixing improves mass transfer and reaction kinetics leading to faster transesterification and higher yield. It saves excess of methanol and catalyst. Excess methanol and catalyst are significant cost factors in biodiesel production. The ultrasonic reactors add cavitational shear to the mixing process. This gives much smaller methanol droplets resulting in improved methanol and catalyst utilization. Therefore, less methanol and catalyst are required. In addition to that, the cavitation influences the reaction kinetics, leading to faster and more complete transesterification.

Besides, there are absorbents on the market that selectively absorb hydrophyllic materials such as glycerol and mono- and di-glycerides. This treatment, followed by an appropriate filter, has been shown to be effective in lowering glycerides and total glycerol levels. The fats and oil industry literature has other bleaching technologies that may also be explored for biodiesel producers. The European specification for sulfur content is much tighter than the U.S. requirement. As a result, a number of producers in Europe are resorting to the use of vacuum distillation for the removal of sulfur compounds from the biodiesel product. By 2006, all U.S. biodiesel must meet new sulfur standards of 15 ppm or less. Filtering is an essential part of all biodiesel production. While feedstocks entering the plant should be filtered to at least 100 μm, biodiesel leaving the plant should be filtered to at least

5 μm to ensure there is no contaminants are carried with the fuel that could damage the engine.

Manufacturing biodiesel from vegetable oils such as sunflower oil, palm oil jatropha or animal fats, involves the transesterification of fatty acids with methanol or ethanol to give the corresponding methyl esters or ethyl esters. Glycerin is an inevitable byproduct of this reaction. Vegetable oils as animal fats are triglycerides composed of three chains of fatty acids bound by a glycerin molecule. Chemically, triglycerides are called esters. Esters are acids, like fatty acids combined with an alcohol. In the conversion process, triglyceride esters are turned into alkyl esters using a catalyst and an alcohol reagent such as methanol which yields methyl esters biodiesel. The methanol replaces the glycerin while the glycerine which is the heavier phase, will sink to the bottom. On the other side, biodiesel the lighter phase floats on top and can be separated, by centrifugal separator. This conversion process is called transesterification process. Figure 1.1 below shows the reaction of triglyceride with methanol.

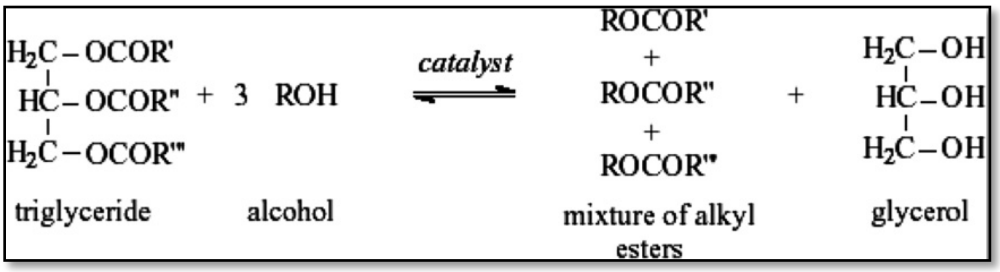

Figure 1.1: Transesterification of triglycerides

Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. The reaction is shown in Figure 1.1. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product.

Conventionally, the strong basic or acidic solutions such as NaOH, KOH and H_2SO_4 are used as a catalyst and food-grade vegetable oils as raw material according to Soriano *et al*. (2009). These homogeneous catalysts are quite sensitive to free fatty acids (FFA) and water in the oil feedstocks and alcohols. While the base-catalyzed transesterification of vegetable oil or animal fat is the most adopted technology for biodiesel commercial production, the process makes the biodiesel of higher manufacturing cost compared to petroleum-based diesel fuel. The process is sensitive to the quality of the feedstock requiring vegetable oil or animal fat with very low amount of free fatty acid (FFA).

1.2 Problem Statement

The main purpose to continue this study is because of the headlines of the current issue involve the renewable resources, petroleum based fuel and global warming. Renewable energy plays an important role in the supply of energy. When renewable energy sources are used, the demand for fossil fuels is reduced. Generally, the production and use of renewable fuels has grown more quickly in recent years due to higher prices for oil and natural gas, and a number of State and Federal Government incentives, including the Energy Policy Acts of 2002 and 2005. The use of renewable fuels is expected to continue to grow over the next 30 years, although people still rely on non-renewable fuels to meet most of our energy needs.

Chemically, transesterification is taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acid, removing the glycerin and creating and alcohol ester. The advantage in using transesterification process is reducing the viscosity of vegetable oil. In the industry, common conventional catalyst used such as NaOH and KOH formed extensive soap formation as its react with high amounts of FFA via a saponification reaction. Soap renders biodiesel purification and catalyst removal even more challenging due to the formation of a stable emulsion generating a significant amount of waste water. The presence of high amounts of FFA in the feedstock therefore eventually leads to decreased biodiesel conversion and yield. In fact, studies have demonstrated that the amount of FFA in the feedstock for biodiesel production should not be higher than 0.5% in order to afford a product that passes the ASTM biodiesel standard.

Hence, the most appropriate catalyst is homogeneous Lewis acid which is aluminium chloride ($AlCl_3$). $AlCl_3$ catalyzed the transesterification of vegetable oil far more effectively rather than $ZnCl_2$ since $AlCl_3$ is a strong Lewis acid. It was also demonstrated that $AlCl_3$ could catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA.

1.3 Objectives

The aims of this study are:

i. To determine the conversion of oil using transesterification process catalyzed by homogeneous Lewis acid.
ii. To determine the optimum operating conditions for the reaction.

1.4 Scope of the research

The scopes have been identified for this study in order to achieve the objective of this research:

i. To study the effect of methanol to oil molar ratio.
ii. To study the effect of catalyst concentration.
iii. To study the effect of reaction temperature.

1.5 Significance of the research

The significance of the research is reducing the usage of gasoline by boosting the efficiency of green technology such as biodiesel since it is non-toxic, renewable, biodegradable and also environmental friendly fuel. Besides, the byproduct of this process which is glycerol is mainly used in food, pharmaceutical and cosmetic industries. Moreover, methyl esters have a positive energy balance, that is, the total consumed energy in the production process is lower than the energy that they can provide as fuels. By using homogeneous Lewis acid, large amount of water can be saved. This is because in the conventional method by using sodium or potassium hydroxide, a large amount of waste water was produced to separate and clean the catalyst and the products. Therefore, by using aluminium chloride ($AlCl_3$), there is no such problem will occur and the cost for treat the wastewater can be saved and environment is not an issue.

CHAPTER 2

LITERITURE REVIEW

2.1 Introduction

Diesel fuel is the common term for the motor vehicle fuel used in the compression ignition engines named for their inventor, the German engineer Rudolf Diesel, who has patented his original design in 1892. While diesel engines are capable of burning a wide variety of fuels, diesel fuel refined from crude oil is the most widely used nowadays. Diesel fuel is important to the whole world's economy, quality of life, and industry application. Basically, consumer started to accept the fact that the diesel fuel prices are soaring and someday it will come to an end. As the result, there are a lot of other alternative fuel and also energy sources that have been carried out such as ethanol, natural gas, solar power, wind power, hydrogen and also hydroelectric power.

One of the best alternatives is biodiesel. Chemically, biodiesel can be defined as fatty acid methyl esters, which is derived from triglycerides by transesterification with methanol. The National Biodiesel Board (NBB) which is the national trade association representing the biodiesel industry in the United States, defines biodiesel as a product that typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin as a by-product. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. In addition it can be used in compression-ignition (diesel) engines with little or no modifications. Besides, it is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics.

Technically, biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel contained in the blend (ie: B20 is 20% biodiesel, 80% petroleum diesel). Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751) in order to insure proper performance which ASTM D6751 is a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments. Biodiesel that meets ASTM D6751 and is legally registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel. Table 2.1 show the specification for pure (100%) biodiesel prior to use or blending with diesel fuel.

Table 2.1: ASTM D6751 Biodiesel Specification (2008)

Property	ASTM Method	Limits	Units
Flash point	D93	93 minimum	Degrees °C
Water & Sediment	D 2709	0.05 maximum	% vol.
Kinetic Viscosity, 40°C	D 445	1.9-6.0	mm^2/sec
Sulfated Ash	D 874	0.02 maximum	% mass
Sulfur S 15 Grade S 500 Grade	 D 5453 D 5453	 0.0015 max. (15) 0.05 max. (500)	 % mass (ppm) % mass (ppm)
Copper Strip Corrosion	D 30	130 maximum	
Cetane	D 613	47 minimum	

Cloud Point	D 250	Report	Degrees °C
Carbon Residue 100% sample	D 4530*	0.05 maximum	% mass
Acid Number	D 664	0.50 maximum	mg KOH/g
Free Glycerin	D 6584	0.020 maximum	% mass
Total Glycerin	D 6584	0.240 maximum	% mass
Phosphorus Content	D 4951	0.001 maximum	% mass
Distillation, 90°C	D 1160	360 maximum	degrees °C

2.2 Raw material

Basically, there a two raw material that widely used for biodiesel production which are vegetable oil and animal fats. Usually vegetable oil is the common material that being used.

2.2.1 Animal fats

Theoretically, animal fatty acid esters are usually very cheap but have negative physical properties such as high pour point, high viscosity, high flash point and hard processing. Tashtoush *et al*. (2004) has studied the evaluation and optimization of the conversion for waste animal fat (WAF) into ethyl and methyl ester called biodiesel. The physical and chemical characteristics of these esters were much closer to those of diesel fuel than those of fresh vegetable oil or fat, which makes them a good substitute for diesel fuel. Experiments have been performed to determine the optimum conditions for this conversion process using a three factor factorial design for producing biodiesel. At the end of the research, it can be conclude that WAF is a good raw material for biodiesel production, but 20–25% of this fat is glycerin, which makes them thick and sticky. This glycerin is substituted in a chemical process called transesterification to make the WAFs thinner or to reduce their viscosity.

2.2.2 Vegetable oil

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Generally, vegetable oil is being used instead of animal fats.

2.2.2.1 Virgin oil

Virgin oil feedstock such as soybean and rapeseed are the most common material that has been used. Furthermore, soybean oil itself accounting for about ninety percent of all fuel stocks in United States. It also can be obtained from field pennycress and Jatropha other crops such as mustard, flax, sunflower, palm oil, coconut and hemp. Sunflower oil is being tested in quite a few places worldwide for its biodiesel capability while the chemical properties of the oil lend themselves well for biodiesel manufacture. Antolin *et al*. (2002) has proved that sunflower oil does not have one fixed quality, but different qualities depending on weather conditions and agricultural practices, and that intraspecific variation in biodiesel quality can be larger than interspecific differences in his simulation experiment of variability of sunflower oil in biodiesel production.

The simulations using a validated model showed that, sunflower oil from high-oleic hybrids is suitable for biodiesel production, regardless of growing conditions and sunflower oil from traditional hybrids is suitable for biodiesel production under the standards of Argentina and US, while only certain hybrids grown in warm regions such as Northern Argentina, Southern US, China, India, and Pakistan are suitable for biodiesel production according to the European standard. Based on Table 2.2 below, it shows the fatty acid composition of vegetable oil samples that usually used in this study of biodiesel while for Table 2.3 below, it shows the physical properties and also the compositions of the sunflower oil that has been used as the raw material in this experiment.

Table 2.2: Fatty acid composition of vegetable oil samples

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Rapeseed	3.5	0	0.9	64.1	22.3	8.3	0
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Peanut kernel	11.4	0	2.4	48.3	32.0	0.9	4.0
Walnut kernel	7.2	0.2	2.6	18.5	56.0	16.2	0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut	7.8	0.1	3.0	4.4	0.8	0	65.7
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9

Table 2.3: Physical properties and composition of sunflower oil

Physical state and appearance	Liquid
Molecular weight	887 g/L
Colour	Light yellow
Composition	• Palmitic acid : 4 – 9 % • Stearic acid : 1 – 7 % • Oleic acid : 14 – 40 % • Linoleic acid : 48 – 74 %
Density	917 kg/m^3
Smoke point (refined)	232°C

Smoke point (unrefined)	227°C

2.2.2.2 Waste vegetable oil

Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world. Besides, there are a lot of disadvantages are using waste vegetable oil which will thickening the fuel, cause gumming in engine, acid in waste vegetable oil will damage the fuel system and if has been used in along time, it may become hydrogenated and the acidity will increase.

2.2.2.3 Waste cooking oil

In this context, waste cooking oil is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment. Besides, it reduces the need to use land for biodiesel producing crops. Waste cooking oils are currently collected from large-scale food processing and service facilities. In fact, the quantities of waste cooking oils available for biodiesel production in Europe are relatively high. The amount of waste cooking oil collected for recycling in the Europe is estimated to be approximately 0.7–1.0 million tonnes per year. Traditionally, these waste oils were used as an additive to animal feed. However, many harmful compounds are produced during the frying of vegetable oils. Awareness of this problem results in banned the use of waste cooking oils in the composition of animal feed in 2002. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids.

Biodiesel production for waste cooking oil has been previously studied. Kulkarni and Dalai (2006) published an excellent review of biodiesel production processes from waste cooking oils. The soap formation using alkaline catalyst is an undesirable side reaction, because it partially consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps. For this reason, the methanolysis of waste cooking oils using an acid catalyst like sulphuric, hydrochloric or sulfonic acid has also been reported since soap formation can be avoided by using this type of catalyst. Furthermore, the above acids catalyze the free fatty acid esterification to produce fatty acid methyl esters, increasing the biodiesel yield. Nevertheless, the acid-catalyzed transesterification is much slower than the basic catalyzed reaction and also needs more extreme temperature and pressure conditions. Table 2.4 shows the common raw material that usually being used in biodiesel manufacturing.

Table 2.4: Raw material used in biodiesel production

Raw materials	Findings	References
1. Waste animal fats	• Temperature had no detectable effect on the ultimate conversion ratio and viscosity for both ester products. • However, higher temperatures decreases the time required to reach maximum conversion, which will be at the expense of the cost of energy. • Besides animal fats, is good raw material for biodiesel production, but 20–25% of this fat is glycerin, which makes them thick and sticky. • Animal fat reacts very sensitive if too much catalyst is used. Soap will formed and cause whole mixture turns into some kind of thick glob, which results in production loss.	Tashtoush *et al.* (2004)
2. Virgin oil	• Optimisation of the most important variables such as temperature	Antolin *et al.* (2002)

	conditions, reactants pro- portion and methods of purification, with the purpose of obtaining a high quality biodiesel that fulfils the European pre legislation with the maximum process yield. • Finally, sunflower methyl esters were characterised to test their properties as fuels in diesel engines, such as viscosity, flash point, cold filter plugging point and acid value. Results showed that biodiesel obtained under the optimum conditions is an excellent substitute for fossil fuels. • Sunflower methyl esters, whose characteristics as fuel in diesel engines are within the specifications of the current Eu-ropean pre-legislation, has been obtained, duly fulfilling the main demanded parameters. These char-acteristics are density, viscosity, flash point and sulphur content, which also present good values of calorific power and cetane index.	
3. Waste cooking oil	• The conversion of free fatty acids of WCO into FAME in the two-step method was 97.22% at the reaction time of 4 h, mole ratio of methanol to TG of 10:1, compared in the acid method with 90%, 10 h, and 20:1, respectively, showing much higher	Yong *et al.* (2006)